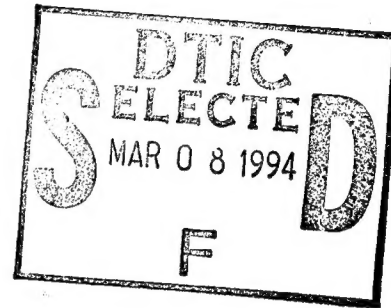


## The Effects of Platinum on Nickel Electrodes in the Nickel Hydrogen Cell

1 March 1995



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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. F04701-88-C-0089 with the Space and Missile Systems Center, 2430 E. El Segundo Blvd., Suite 6037, Los Angeles AFB, CA 90245-4687. It was reviewed and approved for The Aerospace Corporation by T. A. Galantowicz, Principal Director, Electronics Technology Center.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

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# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1 March 1995		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE The Effects of Platinum on Nickel Electrodes in the Nickel Hydrogen Cell				5. FUNDING NUMBERS  F04701-88-C-0089	
6. AUTHOR(S)  Zimmerman, Albert H.					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Aerospace Corporation Technology Operations El Segundo, CA 90245-4691				8. PERFORMING ORGANIZATION REPORT NUMBER  TR-0091(6945-01)-1	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Space and Missile Systems Center Air Force Materiel Command 2430 E. El Segundo Blvd. Los Angeles Air Force Base, CA 90245				10. SPONSORING/MONITORING AGENCY REPORT NUMBER  SMC-TR-95-4	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT  Approved for public release; distribution unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Under conditions of nickel precharge in nickel hydrogen cells, it is possible for platinum complex ions to form at the platinum catalyst electrode when no hydrogen is present. Platinum complex ions have been shown to interact with the active material in the nickel electrode to catalyze the formation of a nickel-cobalt compound within the active material lattice. This compound is readily identified by its characteristic voltage signature. A mechanism for the formation of this compound is proposed, and the effects that this compound has on the performance of the nickel electrode in the nickel hydrogen cell are described.					
14. SUBJECT TERMS Batteries Nickel Hydrogen Platinum				15. NUMBER OF PAGES 32	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT		

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## I. INTRODUCTION

The performance of the nickel electrode used in nickel hydrogen cells has been affected by the incorporation of additives and dopants in the electrode, and by other variations in the solid-state structure of the active material in the electrode. For example, performance has been affected by the use of cobalt additives in the nickel hydroxide active material, by the incorporation of potassium or lithium [1] into the gamma-NiOOH charged material, and by the interaction of hydrogen gas itself with the nickel electrode [2,3]. Numerous reactions are then possible that can result in changes to the active material, depending on conditions of cell potential and state of charge. This study addresses the possible interactions of platinum and platinum compounds with the nickel electrode that are possible in the nickel hydrogen cell, where both the nickel electrode and a platinum catalyst hydrogen electrode are in intimate contact with the alkaline electrolyte.

Normal operation of the nickel hydrogen cell maintains the nickel electrode at highly oxidizing potentials and the hydrogen electrode at quite reducing potentials. Under these conditions, the only possible path for platinum to interact with the nickel electrode is by physical transfer of platinum catalyst particles from the hydrogen electrode, through the separator, to the nickel electrode. Such transfer, which may occur by "popping," can leave platinum catalyst particles in contact with the nickel electrode. (Popping is the explosive reaction between bubbles of oxygen gas and hydrogen gas at the platinum catalyst surface of the hydrogen electrode. This reaction can occur when a nickel hydrogen cell is in overcharge if there is sufficient electrolyte in the separator to enable oxygen to gather into bubbles.) Such particles of platinum are then oxidized at the nickel electrode to platinum oxide  $\text{PtO}_2$ , by electrochemical reaction [4]. Platinum oxide, however, has some solubility in alkaline solutions [5], resulting in the formation of the platinum complex ion  $\text{Pt}(\text{OH})_6^-$ . The platinum is likely to eventually

be replated back onto the platinum catalyst hydrogen electrode by electrochemical reduction of the dissolved platinum species. However, until the slow transfer of platinum back to the hydrogen electrode occurs, both the  $\text{PtO}_2$  and  $\text{Pt(OH)}_6^-$  species can be present in the nickel electrode for possible interactions with the active material.

In addition to the normal operating conditions just described, storage is another condition that the nickel hydrogen cell may be experiencing for considerable periods of time. During storage, the cell is typically discharged and either open circuit or short circuited. With a hydrogen precharge in the cell, both the nickel and hydrogen electrodes develop a quite reducing potential, resulting in stability of the platinum metal at both electrodes. During storage, it is thus unlikely that platinum will react with active nickel electrode material in a hydrogen precharged cell.

With a nickel precharge in a stored nickel hydrogen cell, the hydrogen electrode rises to the highly oxidizing potential of the nickel electrode as the hydrogen gas becomes depleted in the cell. Since the partially charged nickel electrode maintains a slight oxygen pressure in the cell, the platinum catalyst electrode becomes an oxygen electrode at about the same potential as the nickel electrode. At the oxidizing potential maintained by the nickel electrode, the platinum metal in the catalyst electrode is not thermodynamically stable and can undergo slow oxidation to  $\text{PtO}_2$ . Furthermore, in alkaline solutions, the  $\text{PtO}_2$  will not be effective for passivating the platinum metal, because the oxide is slightly soluble, again giving the  $\text{Pt(OH)}_6^-$  species. This ionic species can then diffuse through the cell electrolyte, making itself available for interactions with the active material in the nickel electrode.

Thus, there is certainly opportunity for both platinum oxides and soluble platinum complex ions to interact with the nickel electrode under a

variety of conditions. The question remains, however, as to whether such interactions are either energetically or kinetically feasible under any of these conditions. Addressing this issue will be the primary purpose of this study.



## II. PLATINUM INTERACTIONS WITH NICKEL ELECTRODES--

### DATA FROM NICKEL HYDROGEN CELLS

Data obtained from a variety of nickel hydrogen cells indicate the formation of a material not previously seen in nickel electrodes. This material can be identified in tests on electrodes removed from nickel hydrogen cells by its unique electrochemical signature during the reduction of residual capacity in the nickel electrode, as indicated in Figure 1. Since the cells from which these electrodes were removed were totally discharged, the existence of residual nickel electrode capacity indicates that this new material (compound x) is only formed in nickel hydrogen cells having a nickel precharge. The amount of compound x typically formed is in direct proportion to the amount of nickel precharge in the cell, as determined by the amount of residual charge in the nickel electrodes.

As indicated in Figure 1, compound x may be recognized by its characteristic reduction at a potential of about 0.15 V vs Hg/HgO in 31% KOH electrolyte. If the electrode potential is increased immediately after reduction, it is possible to apparently re-oxidize at least some of compound x at a potential of about 0.30 V vs Hg/HgO, as indicated in Figure 2. However, it is clear that in reduced form, compound x is not stable. After 24 h at 0.0 V, no compound x remains that can be either oxidized or reduced upon cycling the nickel electrode. This material has apparently decomposed when left in the reduced state. In contrast, the stability of compound x in the oxidized state appears to be quite high. Repetitive cycling of the nickel electrode does not alter compound x, as long as the electrode voltage is kept high enough so that compound x will not be reduced, i.e., above about 0.2 V vs Hg/HgO. Compound x seems to form in the nickel hydrogen cell in material that is never discharged during cell operation. Thus, it is a more stable phase of active material that never undergoes discharge, and the increase in the amount of compound x tends to consume whatever nickel precharge exists in the cell. It should be pointed out that the presence of compound x in nickel

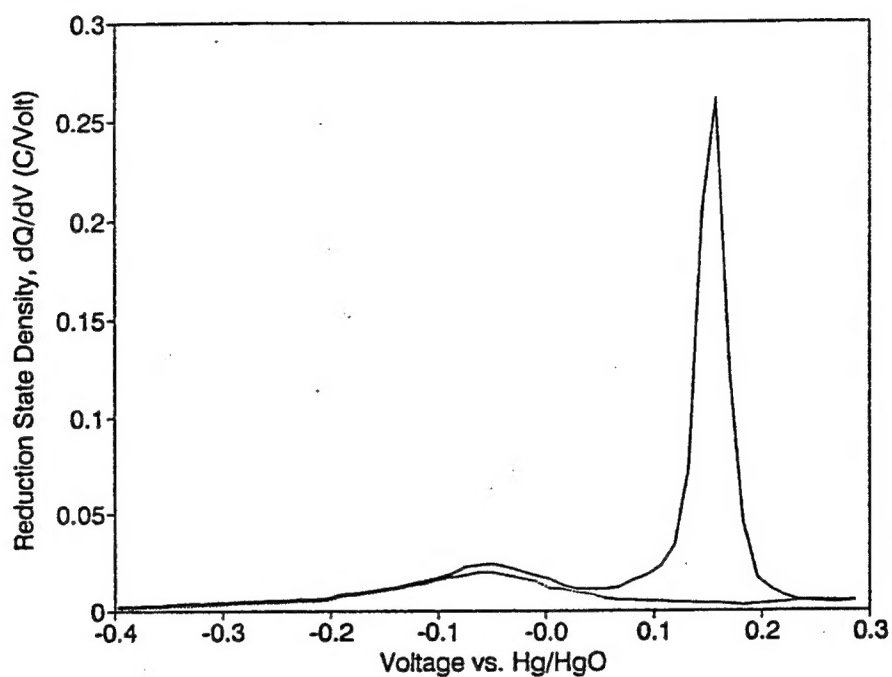


Figure 1. Scan of density of electrochemically reducible states as a function of potential for a  $1 \text{ cm}^2$  nickel electrode from a nickel-precharged nickel hydrogen cell (—) and a new nickel electrode (---). KOH concentration is 31%, and the effective voltage scan rate is  $0.002 \text{ mV/s}$ . Total charge in the peak at about  $0.15 \text{ V}$  is about  $5 \text{ mAh/cm}^2$ .

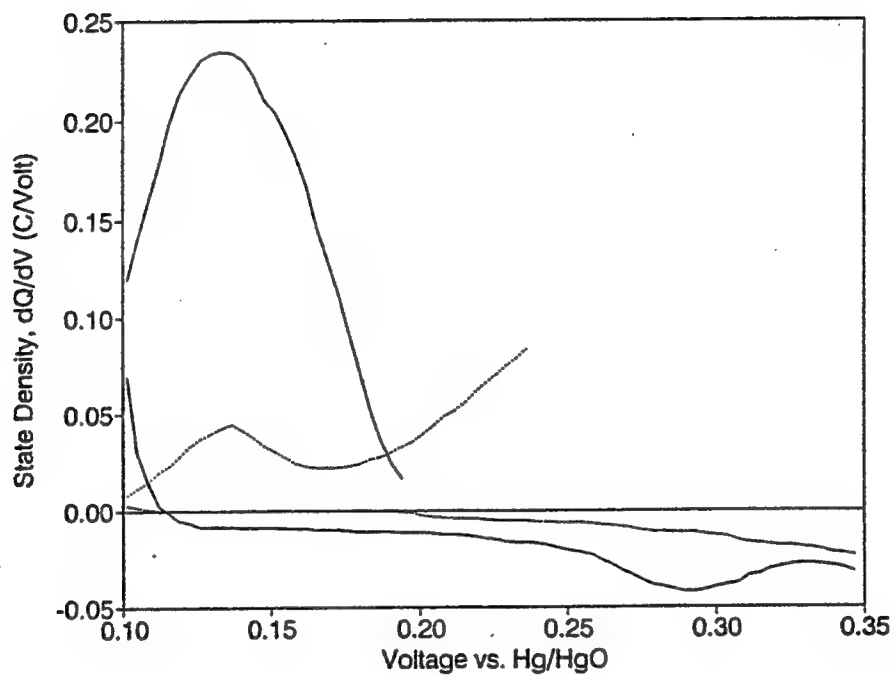


Figure 2. Scans of electrochemically active states as a function of potential for a nickel electrode from a nickel-precharged nickel hydrogen cell; (—) initial reduction and re-oxidation; (---) following one full reduction/oxidation cycle. (Note that a 24 h stand is allowed between reduction and oxidation.) KOH concentration was 31%, and the effective voltage scan rate was 0.002 mV/s.

hydrogen cells is not necessarily a problem; in fact, the cells containing the largest quantities of compound x were some of the best performing cells of a given design that have been made.

In nickel hydrogen cells containing approximately 20% nickel precharge, about 10% of the total capacity of the nickel electrode (about 5 mAh/cm<sup>2</sup>) was present in the oxidized form of compound x. Because this seemed to be a quite large amount of modified active material, x-ray diffraction measurements were done on isolated active material in an attempt to identify the structure of the modified active material. (Active material was isolated from the sinter by grinding it into a fine slurry in DI water, then magnetically separating the nickel metal particles from the active material in water solution. The active material was then filtered from the solution and dried.) The x-ray diffraction patterns of this material, however, indicated no significant differences between active material from new nickel electrodes and that from the nickel electrodes containing compound x. Spectrographic chemical analysis of the bulk active material indicated that the only unexpected contaminant present in significant quantities was platinum, which constituted about 0.5% of the total active material weight.

A more precise chemical analysis of the modified active material was done by leaching the normal active material from the electrodes containing compound x and analyzing the residue left behind. The normal active material was dissolved in 10% acetic acid at 70°C. The residue left after this dissolution process was filtered, washed, and dried. Analysis of the residue was done using energy dispersive analysis by x-rays (EDAX), x-ray diffraction, and spectrographic analysis. The x-ray diffraction results were of little use, since no well-defined diffraction peaks could be seen, except those from small fragments of the zircar separator used in the nickel hydrogen cell. This result indicated that the compounds making up this residue were essentially amorphous rather than crystalline. EDAX analysis of the residue revealed that its major constituents were Ni, Co, Pt, and oxygen. The platinum was not present in the metallic state as catalyst particles but was

uniformly dispersed throughout the residue, most likely in the form of an oxide. Every part of the residue analyzed by EDAX had essentially identical proportions of Ni, Co, Pt, and oxygen.

The composition of the residue was determined using semi-quantitative spectrographic analysis. The weight percentages of each element found in the residue are indicated in Table 1. Consistent with the EDAX results, the primary constituents were Ni, Co, Pt, and oxygen, with smaller amounts of zirconium oxide (from the cell separator), silicates, and iron.

Table 1. Elemental Composition of Nickel Electrode Residue

Element	Weight percent	Atom percent
Ni	25.2	19.1
Co	27.2	20.6
Pt	25.5	5.8
O	18.8	52.4
Zr	2.5	1.2
Si	0.3	0.5
Fe	0.5	0.4

It is assumed that the nickel electrode residue bears some relationship to the composition of compound x, suggesting that this compound is some oxide of Ni, Co, or Pt. The amount of charge associated with compound x (from electrochemical measurements) was about 5% of the total electrode capacity. Therefore, the amount of Pt found in the active material would have to undergo transfer of about 10 electrons per platinum atom if a platinum oxide were to be responsible for compound x. Clearly this is impossible, indicating that if Pt is involved in compound x at all, it is as a binary or ternary oxide with cobalt or nickel.

The redox potentials observed for compound x provide a signature that is characteristic of the specific compound undergoing redox reactions and thus can be used to help identify compound x, assuming it is not a heretofore unknown material. Detailed review of redox potentials for oxides of Ni, Co, and Pt, as well as binary or ternary combinations of these elements, revealed only one compound having redox potentials consistent with those observed for compound x [6]. This compound has a nominal formulation of  $\text{NiCoO}_2(\text{OH})_2$ , based on the preparation of this compound [6] by co-precipitation and oxidation of mixed nickel and cobalt hydroxides. This compound is also quite consistent with the residue analysis results of Table 1, where Ni and Co are present in about a 1:1 ratio. The platinum is likely to be present as a highly dispersed oxide mixed with the  $\text{NiCoO}_2(\text{OH})_2$ .

While the identification of compound x as  $\text{NiCoO}_2(\text{OH})_2$  appears to be fully consistent with the available chemical and electrochemical data from modified nickel electrodes, the detailed mechanism by which this compound forms and the role, if any, of Pt in this mechanism is not clear. In addition, a number of details related to the electrochemical performance of the modified nickel electrodes are not fully consistent with this simple picture of an isolated  $\text{NiCoO}_2(\text{OH})_2$  phase somehow being separated from otherwise stable active material. First, if 10% of the electrode capacity is present as  $\text{NiCoO}_2(\text{OH})_2$ , as was observed in extreme cases for electrodes containing 5% Co additive, then essentially all the cobalt has separated from the normal active material and has been incorporated into this modified phase. The loss of all cobalt from the remaining 90% of the active material should result in both significant increases in redox potentials [6] and significant decreases in electrochemical utilization. Neither of these effects is seen. As indicated in Figure 3, very little shift in potential for the 90% "normal" active material is seen, and, if anything, the utilization of this material is significantly increased relative to the utilization in an unmodified electrode. The only significant modified characteristic for the normal charge/discharge processes is that the modified active material seems to be

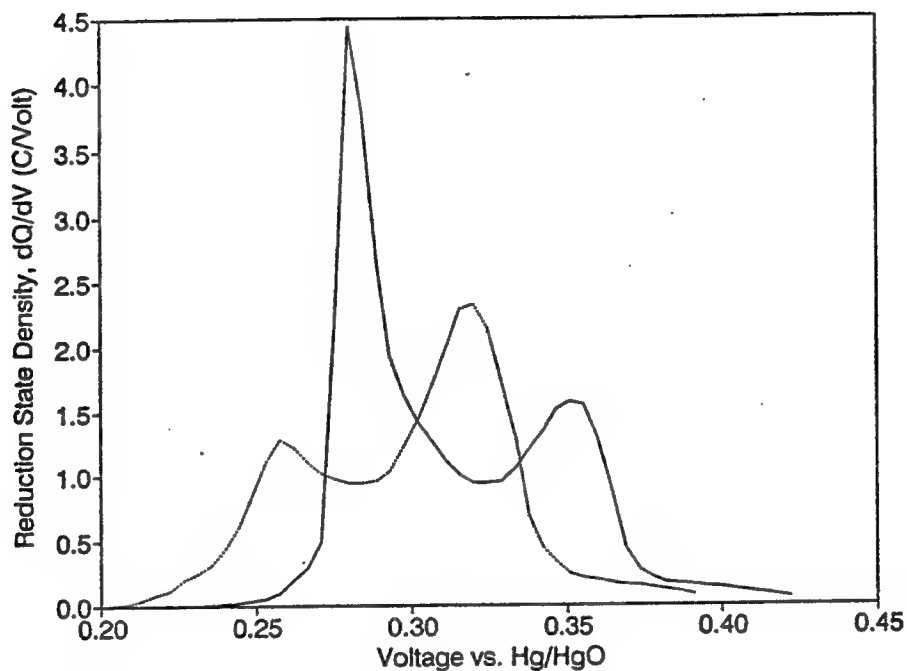


Figure 3. Comparison of the density of reducible states for normal discharge of the capacity in a new nickel electrode (—) and an electrode from a nickel-precharged nickel hydrogen cell (---). KOH concentration was 31%, and the effective scan rate was 0.002 mV/s. Prior to this reduction, each electrode was oxidized to 0.5 V at this same effective voltage scan rate.

much more readily charged into the gamma-NiOOH phase, which discharges at potentials about 30 mV lower than the beta-NiOOH phase (see Figure 3). The primary goal of the remainder of this study is to resolve these apparent inconsistencies, and to understand the mechanism and impact of  $\text{NiCoO}_2(\text{OH})_2$  formation in nickel hydrogen cells.



### III. MECHANISM OF $\text{NiCoO}_2(\text{OH})_2$ FORMATION IN NICKEL HYDROGEN CELLS

Detailed studies were necessary to explore the mechanism by which nickel electrode active material is modified to form  $\text{NiCoO}_2(\text{OH})_2$  in nickel-precharged nickel hydrogen cells. Before these studies could begin, laboratory conditions had to be identified under which this compound could be produced from normal active material. Because platinum oxides were always found in modified active material, it was assumed that platinum species played some role in the reactions that occurred.

Initial tests simply involved placing a nickel electrode in 38% KOH with a nickel sheet counter electrode and adding powdered platinum hydroxide or platinum oxide to the electrolyte. The nickel electrode was then continuously charged for 2 weeks at  $0.2 \text{ mA/cm}^2$ . After the 2 weeks, the nickel electrode was removed from this cell, placed in a test cell with 31% KOH and a reference electrode, and reduced, as shown in Figures 1 and 2. With either platinum hydroxide or platinum oxide in the electrolyte, no evidence for nickel electrode active material modification was found. The only significant results were that after 2 weeks with these platinum compounds present in the electrolyte, the nickel counter electrode was coated with a uniform layer of platinum metal. This result confirms that these platinum compounds dissolve slightly in KOH electrolyte and that the  $\text{Pt}(\text{OH})_6^-$  solution species is readily reduced to Pt metal by electrochemical processes.

The nickel electrode environment during storage of nickel-precharged nickel hydrogen cells was then better simulated by placing a nickel electrode in a partially charged state in contact with a zircar separator and a platinum black catalyst electrode. The atmosphere over this simple cell was set to contain the ambient 0.2 atm of oxygen gas. All simulated cells were then wetted with KOH electrolyte and sealed in plastic containers while the reactions were allowed to occur. Initial simulations used nickel electrodes charged to 30, 60, 80, and 100% states of charge in 38% KOH in these test cells. After 30 days of stand time in a test cell, each nickel electrode was

reduced, as shown in Figures 1 and 2. No evidence for modification of the active material was found for any of these nickel electrodes.

A truly accurate simulation of the storage condition of a nickel-precharged nickel hydrogen cell must simulate the solid-state phase structure of the active material that is present in the oxidized and reduced materials that exist when the cell goes into storage. The state of the precharged active material consists of whatever active material remains undischarged following numerous charge/discharge cycles. As such, this material is the most stable, or lowest, potential active material phase present in the nickel electrode. To simulate this situation, a nickel electrode was cycled 100 times in 38% KOH electrolyte. Each cycle involved discharge of 70% of the 20 mAh/cm<sup>2</sup> rated capacity at 10 mA/cm<sup>2</sup>, followed by recharge at 2 mA/cm<sup>2</sup>, to a charge return of 125% of the capacity discharged. After 100 cycles, the 70% discharged electrode was put into a sealed storage condition with a platinum catalyst electrode wetted with 38% KOH electrolyte. After 60 days of storage, the nickel electrode was removed and reduced in 31% KOH, as shown in Figures 1 and 2, to determine whether any modification had occurred to the active material. The results are indicated in Figure 4. These results clearly show some modified active material had formed, as recognized by the peak at about 0.15 V during electrode reduction.

A repeat of the preceding test involved cycling a nickel electrode in 31% KOH electrolyte, instead of in 38% electrolyte, 100 times. In this case, after 4 weeks of storage with a Pt electrode, the somewhat different reduction behavior indicated in Figure 4 was obtained. A reduction peak is seen at about 0.22 V vs Hg/HgO, suggesting that either the active material structure that can undergo modification is quite sensitive to KOH concentration or that 4 weeks was insufficient time to fully modify the active material.

Based on these exploratory studies, a parametric matrix of 32 nickel electrodes was prepared as in the preceding test. The electrodes were cycled 100 times in 38% KOH and were then placed in a sealed storage cell in contact with platinum black electrodes. For control purposes, two electrodes were also stored without a platinum electrode. The variables that were included in

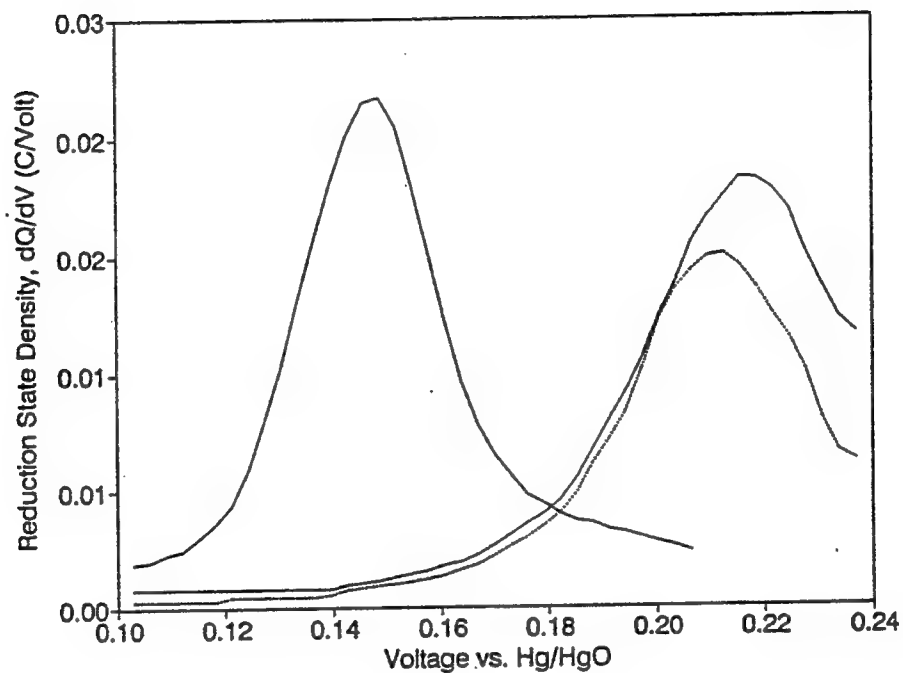


Figure 4. Density of reducible states after storage of nickel electrodes with Pt electrodes in KOH after several different electrode preparation methods; (—) 100 cycles in 38% KOH followed by storage; (—) 100 cycles in 31% KOH ( $\times 0.1$ ) followed by storage; (—) electrode of Figure 1 after 2 years of dry storage ( $\times 0.25$ ). Measurements used an effective voltage scan rate of 0.002 mV/s and were done in 31% KOH.

this parametric study were (1) storage time, 39 to 157 days; (2) storage temperature, 0, 20, and 40°C; (3) cobalt concentration in the active material, 0, 5, and 10%; and (4) electrolyte concentration during storage, 31, 38, and 45% KOH. After various storage times, electrodes were removed from the stored cells and reduced using the same method indicated in Figures 1 and 2. Modified active material was detected, when present, by the observation of a reduction peak near 0.15 V in 31% KOH. The quantity of  $\text{NiCoO}_2(\text{OH})_2$  that was present in each electrode was evaluated from the number of coulombs of charge required to fully reduce the  $\text{NiCoO}_2(\text{OH})_2$  material. To evaluate the effect of KOH concentration on the redox potential for  $\text{NiCoO}_2(\text{OH})_2$  reduction, some electrodes were reduced in test cells containing either 26 or 38% KOH electrolyte.

It was expected that there would be some variation in the amount of  $\text{NiCoO}_2(\text{OH})_2$  formed as a function of storage time. However, as indicated in Figure 5, there was no clear correlation with storage time from 39 to 157 days. The amount of this modified phase found in 5% Co containing electrodes varied from quite small amounts up to quite high levels, irrespective of the storage time allowed. It appears that the amount of this material formed depends on the amount of active material formed in a phase structure that can be readily converted to  $\text{NiCoO}_2(\text{OH})_2$ , an amount that seemed to vary quite widely for different electrode samples.

Figures 6 and 7 indicate the relationships between the amount of  $\text{NiCoO}_2(\text{OH})_2$  formed in nickel electrodes, and the KOH concentration and temperature during storage. Within the range of data, there is no clear dependence on either of these two variables. Figure 8 indicates the dependence of  $\text{NiCoO}_2(\text{OH})_2$  formation on the amount of cobalt additive in the active material. As would be expected, this compound is not formed at all when there is no cobalt present in the active material. The amount of material that is formed increases sharply as the cobalt level in the active material goes from 5 to 10%.

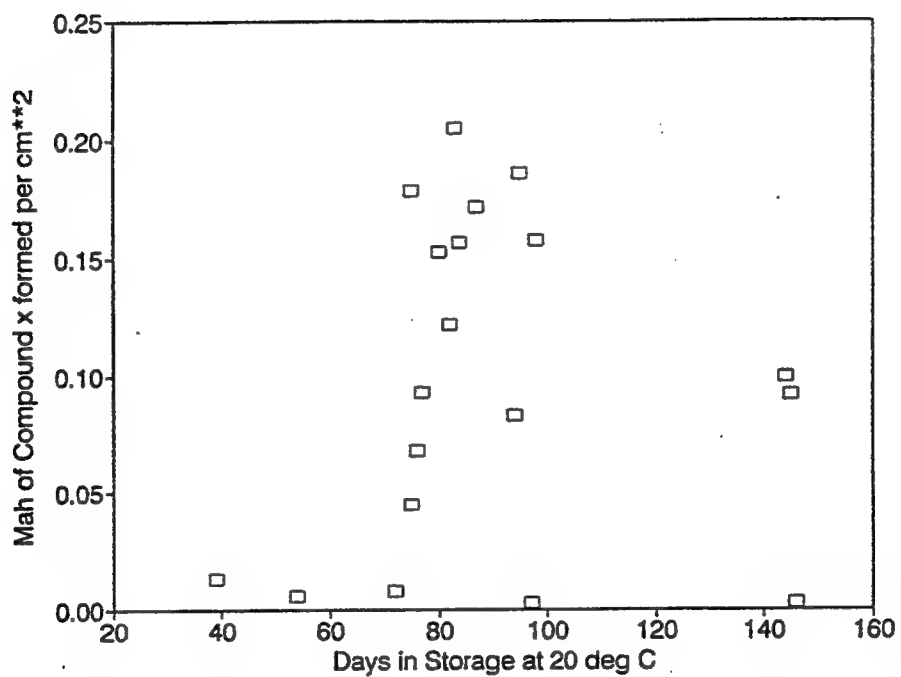


Figure 5. Amount of modified active material formed in nickel electrodes during cell storage as a function of storage time at 20 C, 38% KOH during storage, and 5% Co additive.

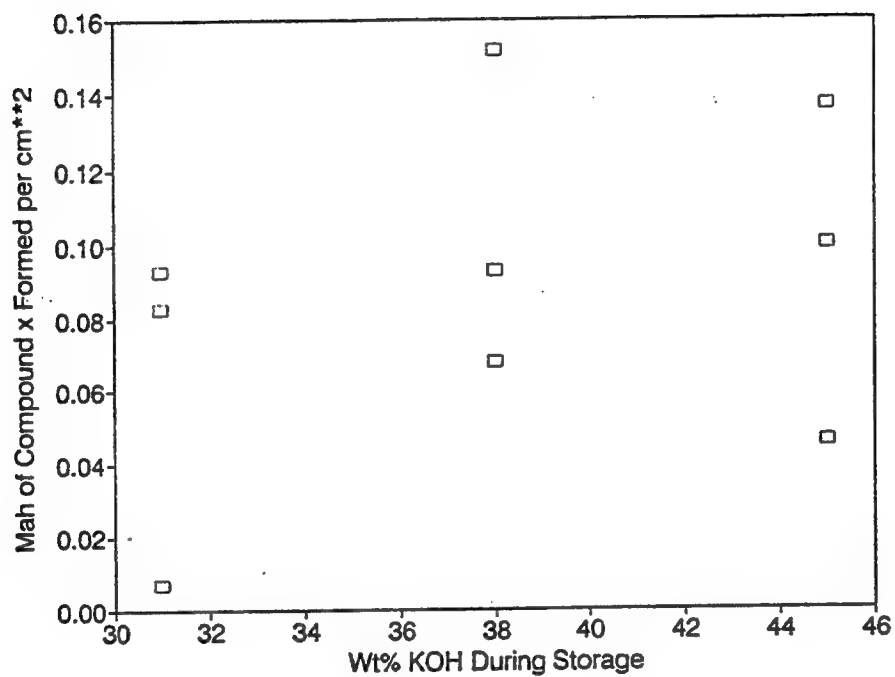


Figure 6. Amount of modified active material formed in nickel electrodes during cell storage as a function of KOH concentration during storage, at 20 C, with 5% Co additive.

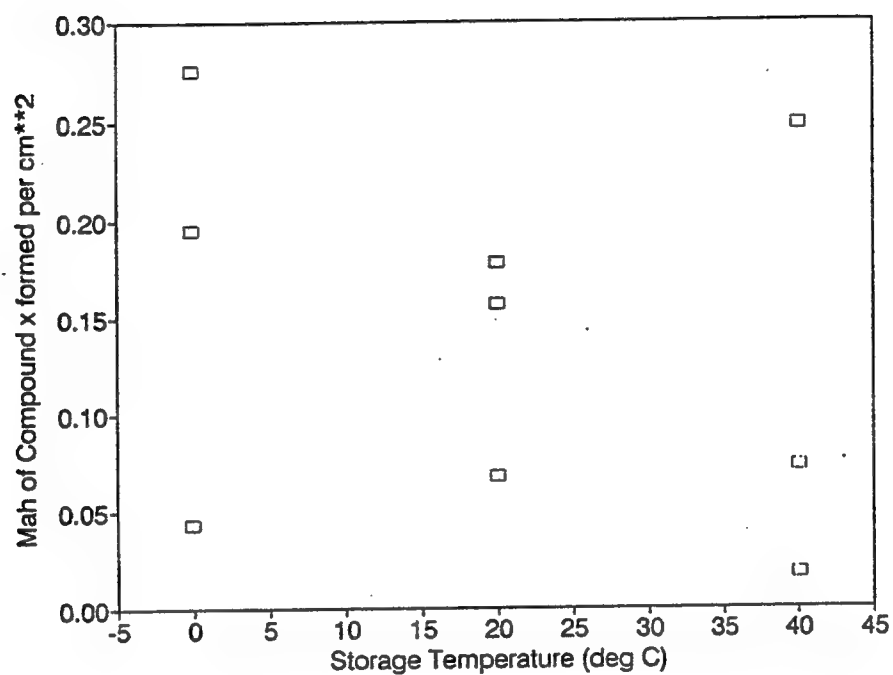


Figure 7. Amount of modified active material formed in nickel electrodes during cell storage as a function of storage temperature, 38% KOH during storage, and 5% Co additive.

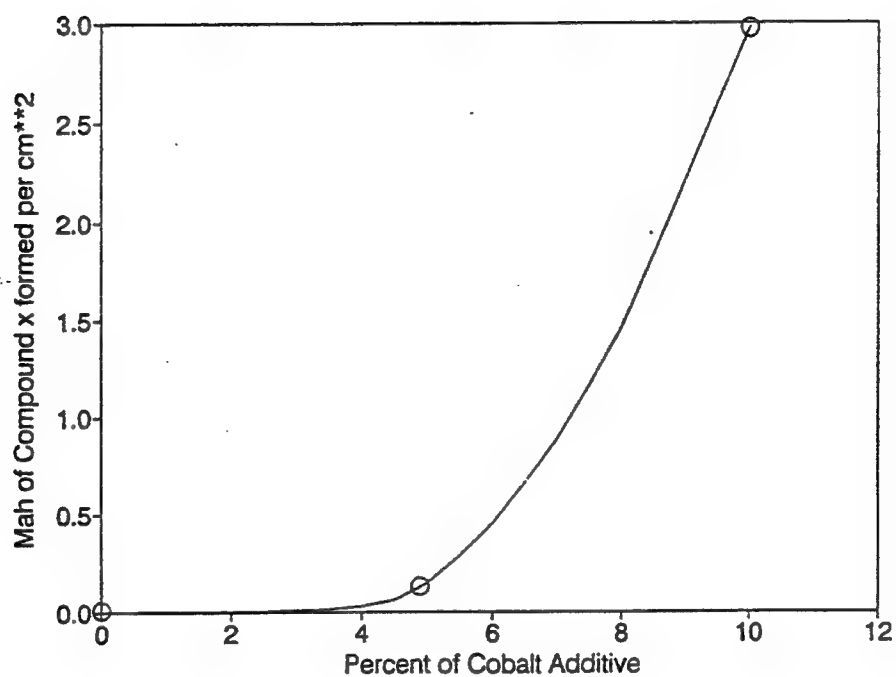


Figure 8. Average amount of modified active material formed in nickel electrodes during cell storage as a function of amount of Co additive. For the 10% Co electrodes, the total electrode capacity was about 30 mAh/cm<sup>2</sup>, indicating that every cobalt atom was incorporated into modified material.



The dependence of the reduction potential of  $\text{NiCoO}_2(\text{OH})_2$  on electrolyte concentration is indicated in Figure 9, where at each concentration, the average reduction potential for several electrodes was used. The observed dependence of reduction potential in Figure 9 on KOH concentration clearly indicates that hydroxide ions are involved in the rate-limiting step of the reduction process. These observations, as well as the observation that no  $\text{NiCoO}_2(\text{OH})_2$  was formed in the control electrodes after up to 75 days of storage, allow a hypothesis to be developed concerning the mechanism for the formation of  $\text{NiCoO}_2(\text{OH})_2$  in nickel electrodes.

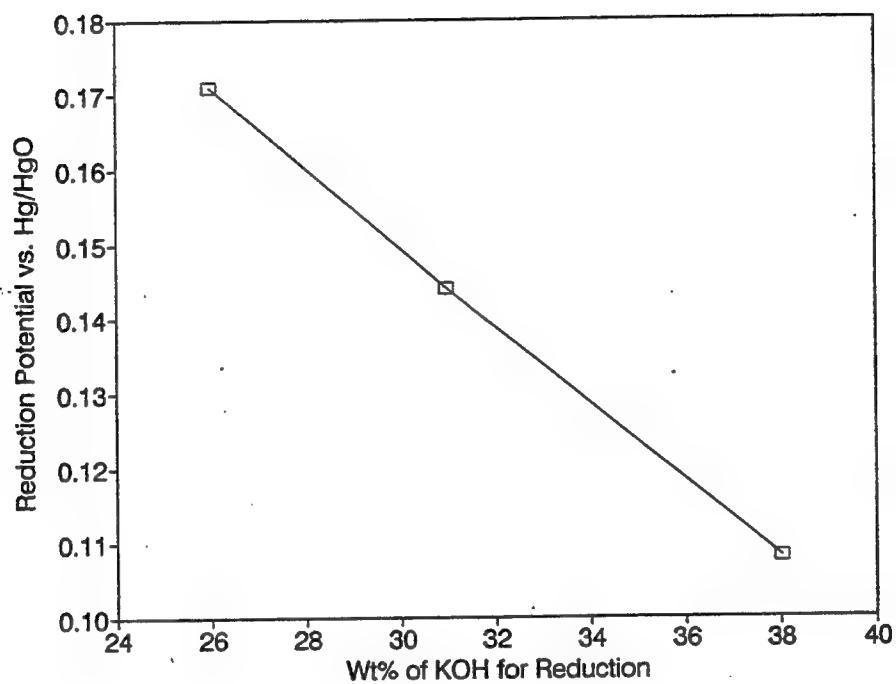
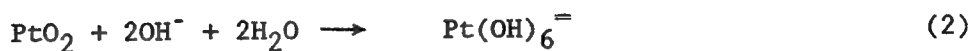
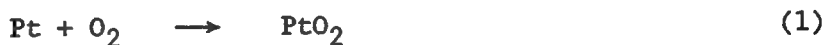


Figure 9. Reduction potential at 20° C for the modified active material phase formed during cell storage as a function of KOH concentration. The electrolyte in the reference electrode was maintained the same as that in the test cell for these measurements.

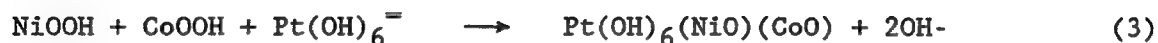
#### IV. POSTULATED REACTION MECHANISM

The fact that  $\text{NiCoO}_2(\text{OH})_2$  is not found to form in the nickel electrode, except when the electrode shares electrolytic contact with oxidized platinum metal surfaces, indicates that platinum species are clearly involved in the reaction mechanism. Because the reaction only requires contact with electrolyte that is also in contact with platinum metal at oxidizing potentials, it is concluded that the  $\text{Pt}(\text{OH})_6^-$  ionic species catalyzes the formation of  $\text{NiCoO}_2(\text{OH})_2$  from the oxidized nickel and cobalt oxyhydroxides in the solid-state lattice. This solid-state catalytic process results in the  $\text{NiCoO}_2(\text{OH})_2$  compound because this is a more energetically stable structure. However, for this catalytic process to occur at a significant rate, it is necessary that adjacent Ni and Co centers in the oxidized lattice have the proper physical proximity. This is why it is key that the proper phase structure be formed in the active material before  $\text{NiCoO}_2(\text{OH})_2$  can form. The proper phase structure is clearly related to the gamma- $\text{NiOOH}$  structure, although the specific structural requirements needed for the gamma- $\text{NiOOH}$  structure to engage in this reaction are not fully clear. It is possible that the lattice configuration involved in such reconfiguration may involve unique interlayer cobalt sites that have been suggested in recent EXAFS studies [7].

A sequence of reactions may be postulated to give  $\text{NiCoO}_2(\text{OH})_2$  in the nickel electrode. First, platinum dissolution in an oxidizing environment produces  $\text{Pt}(\text{OH})_6^-$



The ionic platinum species can then diffuse to the nickel electrode, where they can react with adjacent Ni and Co centers in the solid-state lattice. This reaction is facilitated by the adjacent Ni and Co centers having the necessary geometry to form a complex with the octahedral platinum ions, according to reaction (3)



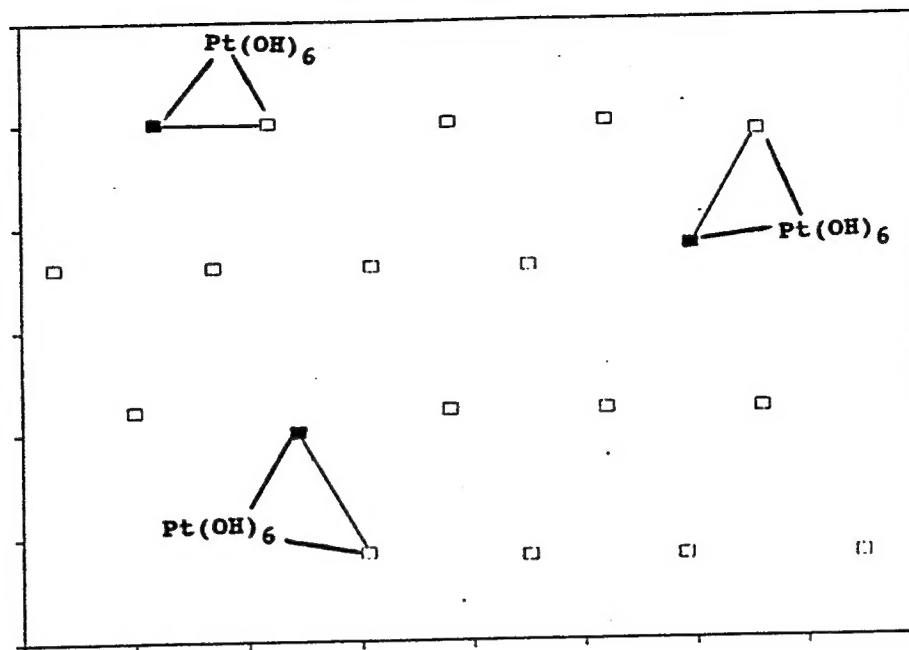
This platinum complex is in equilibrium with the ionic platinum species in solution. Therefore, if the platinum is plated back onto the hydrogen electrode when a nickel hydrogen cell is brought from storage back into normal operation (or for these test cells, when the nickel electrode is put into a platinum-free solution), the platinum complex formed in reaction (3) will fall apart, leaving the adjacent Ni and Co species associated in a new and more stable compound,  $\text{NiCoO}_2(\text{OH})_2$



These compounds are schematically illustrated in Figure 10.

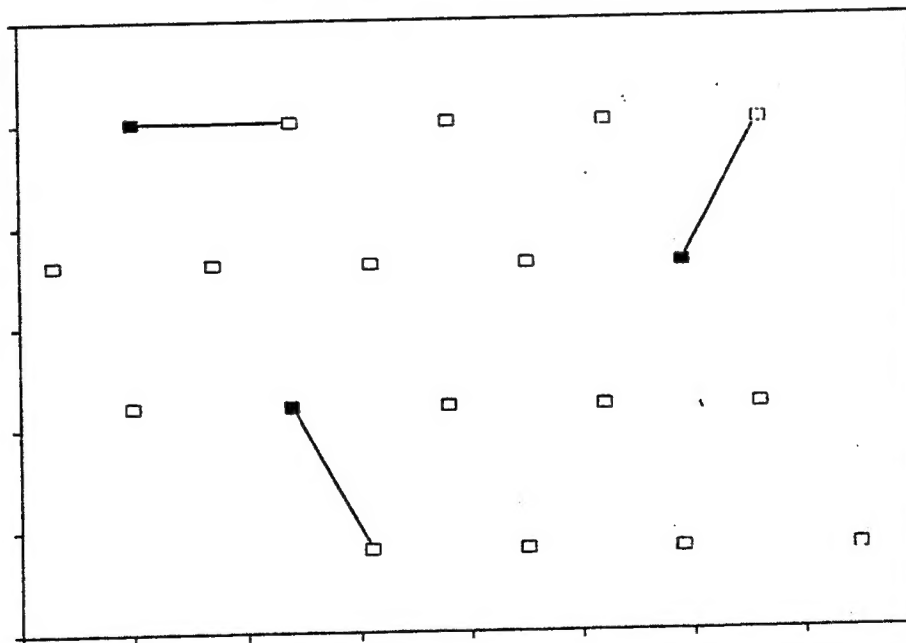
Electrochemical reduction of  $\text{NiCoO}_2(\text{OH})_2$  must at least convert the nickel center to a divalent oxidation state. It is not fully clear whether the cobalt remains in a trivalent oxidation state. However, in any case, it is clear that when these metal species are converted into a reduced oxidation state, the hydroxide structure becomes more stable. The metal species then gradually revert back to a configuration much like their original structure in the solid-state lattice. Thus, there is no irreversible degradation in the active material lattice as a result of these reactions, although the resultant structure does appear to make the lattice more easily oxidized to a gamma-phase active material. The improvement in electrode capacity associated with these reactions is likely to arise from the increased formation of gamma-phase charged material (which has a higher oxidation state) as well as from the electrical conductivity expected for the  $\text{NiCoO}_2(\text{OH})_2$  that is dispersed throughout the active material.

$\text{Pt}(\text{OH})_6(\text{CoO})(\text{NiO})$  Complex



(a)

$\text{NiCoO}_2(\text{OH})_2$  Compound (■ — □)



(b)

Figure 10. Illustrations of possible configurations for (a) platinum-nickel-cobalt oxyhydroxide and (b) nickel-cobalt oxyhydroxide materials in relation to the active material lattice.

## V. CONCLUSIONS

This study suggests that platinum complex ions which can form in nickel precharged nickel hydrogen cells under some conditions can migrate to the nickel electrode, where they can interact with adjacent nickel and cobalt lattice sites that have an appropriate structural configuration. The appropriate lattice configuration appears to require that the active material be in a gamma-phase structure. The configuration may also require a sufficiently large interlayer spacing for platinum ions to penetrate into the active material structure. The platinum complex ions appear to make it energetically possible for adjacent nickel and cobalt centers in the lattice to reconfigure, thus catalyzing the formation of the compound  $\text{NiCoO}_2(\text{OH})_2$  within the lattice. This compound has well-defined redox voltage signatures that allow it to be readily identified in nickel electrodes.

The effects of these reactions on nickel hydrogen cell performance appear to be beneficial, based on cell capacity data and all the electrode performance data presented here. Capacity is improved by making the gamma-phase active material more easily formed during cell recharge, and utilization is also likely to be improved by the added conductivity imparted to the discharged active material by the electrochemically active and highly dispersed  $\text{NiCoO}_2(\text{OH})_2$ . While the effects of these changes on ultimate cell cycle life are not yet fully established, limited life testing of nickel-precharged cells that have also experienced some storage has generally given good results. More intensive life testing in the future will address this issue more fully, as well as the issue of what state these unique compounds eventually end up in late in cell life, when corrosion processes have destroyed the initial nickel precharge in the cell.

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